

A CRITICAL END POINT TO PIGEONITE-AUGITE LIQUIDUS EQUILIBRIA.

J. Longhi¹ and C.M. Bertka², ¹Lamont-Doherty Earth Observatory, Palisades, NY 10964 USA; ²Geophysical Laboratory, 5251 Broad Branch Rd, NW, Washington, DC 20015 USA

Pyroxene liquidus equilibria play an important role in basalt petrogenesis. One of the most important observations in recent years has been the replacement of high-Ca clinopyroxene (cpx) by low-Ca (or "pigeonitic") cpx on the solidus of lherzolitic (olivine-orthopyroxene-clinopyroxene \pm plagioclase/spinel/garnet) mantles with increasing pressure [1]. This observation holds for terrestrial [2], martian [1,3], and lunar [4] compositions. However, the transformation has not yet been tightly constrained by experiments, and the mechanism remains subject to debate. One side proposes that the transition involves a 3-pyroxene reaction ($\text{opx} + \text{aug} = \text{pig}$) and is thus relatively abrupt [1]. The other side advocates involvement of 2-clinopyroxene critical equilibria and thus the transition is more gradual [4]. We now present experimental data and graphical arguments in support of critical phenomena. Regardless of the mechanism, however, partial melting in the presence of low-Ca cpx has important geochemical implications: because of the well-established positive correlation of REE partition coefficients with the Ca content of clinopyroxenes [5], the partition coefficients of cpx will be much lower (\sim opx) at higher pressures than at low pressures where most of the partition coefficients have been measured. Thus many calculations of percent melting and relative proportions of opx and cpx in basalt source regions may need to be reexamined.

The first set of arguments is based upon what is known about shifts in liquidus boundaries with composition and pressure. Fig. 1a (olivine liquidus surface) shows the difference between liquidus boundaries calculated for 1 bar [6] (light solid curves) versus those determined at 30 kbar [4] (heavy dashed curves) for compositions appropriate to primary melts of lunar mare basalt and volcanic glass source regions, i. e. low alkalis and $\text{Mg}'(\text{liq}) = \text{MgO}/(\text{MgO} + \text{FeO}) - \text{molar} = .50-.65$. The 30 kbar experimental data constrain the approximate location of the ol-opx-cpx-gar psuedo-invariant point, the nature of the equilibrium at this point ($\text{opx} + \text{liq} = \text{cpx} + \text{gar} (+\text{ol})$), and the nature of the equilibrium along the ol-opx-cpx liquidus boundary ($\text{opx} + \text{liq} = \text{cpx} (+\text{ol})$). Fig. 1b shows the difference between liquidus boundaries calculated for 1 bar [6] versus those determined at 28 kbar for partial melting of highly depleted terrestrial upper mantle or an undifferentiated magnesian moon [7], i.e. moderate to low alkalis and $\text{Mg}'(\text{liq}) = .65-.75$. The 28 kbar experimental data tightly constrain the composition of the psuedo-invariant point, the nature of the equilibrium at this point (also $\text{opx} + \text{liq} = \text{cpx} + \text{gar} (+\text{ol})$), and the absence of a miscibility gap in cpx composition.

The first (or 3-pyx) model for the appearance of low-Ca cpx on the lherzolite solidus may be thought in terms of the psuedo-invariant points involving opx, aug, and pig (the 3-pyroxene equilibrium) and opx, aug, and plag (the lherzolite solidus) in Fig. 1b migrating together and producing the low-pressure topology in Fig. 1a where pigeonite coexists with opx, plag, ol and liq. Such a migration is well established at constant low-pressure [9], where the $\text{ol} + \text{aug} + \text{plag}$ and $\text{ol} + \text{opx} + \text{plag}$ liquidus boundaries shift toward the Opx-Di join and the $\text{ol} + \text{opx} + \text{pig}$ liquidus boundary shifts away from the Di (or Wo) component with decreasing Mg'. However, the two diagrams in Fig. 1 suggest opposite relative migrations for constant composition and increasing pressure where the pyroxene + olivine + liquid fields expand toward the plagioclase component and where there is a modest relative increase in the Wo component of the $\text{ol} + \text{opx} + \text{pig}$ liquidus boundary. These shifts in liquidus boundaries suggest not only that the B-H model may not apply in highly magnesian systems, but that an opposite effect may apply to low-alkali, intermediate-Mg' compositions, i.e. augite may replace pigeonite on the lherzolite solidus with increasing pressure!

A graphical analysis of liquidus equilibria in the $\text{Mg}_2\text{Si}_2\text{O}_6\text{-CaMgSi}_2\text{O}_6$ system supports these conclusions. Fig. 2 contains two possible P-T arrays of the univariant equilibria: Fig. 2a is consistent with the B-H model; Fig. 2b is consistent with the involvement of critical equilibria. On the right of each figure is a set of schematic isobaric temperature-composition diagrams consistent with the array of univariant curves. The phase relations at 1 bar, although complicated, are known very accurately [e.g., 10,11] and form a rigorous basis for the low-pressure orientations of the equilibria in P-T space. Also, known from experiments and calculations is the slope of the pigeonite (P) - diopside (D) critical curve [8]. Because protoenstatite and olivine are stable only at relatively low pressure in this system, their equilibria are omitted to avoid unnecessary complications, thus some portions of the curves are metastable. Also omitted are possible equilibria involving the liquidus azeotropes: these have second order effects on the equilibria. The major observations are: (i) if the 3 pyroxene curve ($\text{O} + \text{D} = \text{P}$) overtakes one solidus curve, it must overtake the other as well and generate a P-T invariant point; (ii) in the case of the 3-pyroxene invariant point the slopes of the two solidus curves must improbably be steeper than the 3-pyroxene curve; (iii) in order for this invariant point to exist even metastably, the critical curve must be everywhere metastable (Fig. 2a), for if the critical curve stably intersects either the $\text{O} + \text{D} = \text{P}$ curve or the $\text{P} + \text{D} = \text{L}$ curve (points x and y, respectively in Fig. 2b), it will terminate that curve, leaving no metastable extension, thus rendering the invariant point in Fig. 2a impossible; and (iv) if the critical curve stably intersects the $\text{O} + \text{D} = \text{P}$

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curve (point x), then it must intersect the P+D = L curve (point y) at lower pressure. From the experimental work of [12] point x is known to be stable, therefore, y is stable and the 3-pyx mechanism is impossible in this simple system. Examination of the T-X sections shows that the critical equilibrium necessarily produces a super-critical, low-Ca cpx in reaction relation with orthopyroxene and liquid as shown in Fig.1, whereas the 3-pyroxene invariant equilibrium does not. Thus it is likely, but not certain, that the 3-pyx mechanism does not occur under any conditions.

The liquidus expression of the critical phenomena on the olivine liquidus surface of natural systems is a critical end point to the low-pressure pig + aug + ol liquidus curve that emerges from either the opx + ol field or the aluminous phase (probably spinel for most natural compositions) + ol field and with increasing pressure migrates to the Opx-Di join, thus eliminating the pig + aug + ol liquidus curve. Data in the $Mg_2Si_2O_6$ - $CaMgSi_2O_6$ system [8] constrain the maximum stability of this curve to be < 20 kbar (progressively lower pressures with decreasing Mg'). Because the passing of the critical point produces an inflection toward lower Di component in the high-Ca limb of the opx-cpx (supercritical) 2-phase field, the Ca content of cpx coexisting with opx decreases rapidly. Precisely, how rapidly in natural systems remains to be determined.

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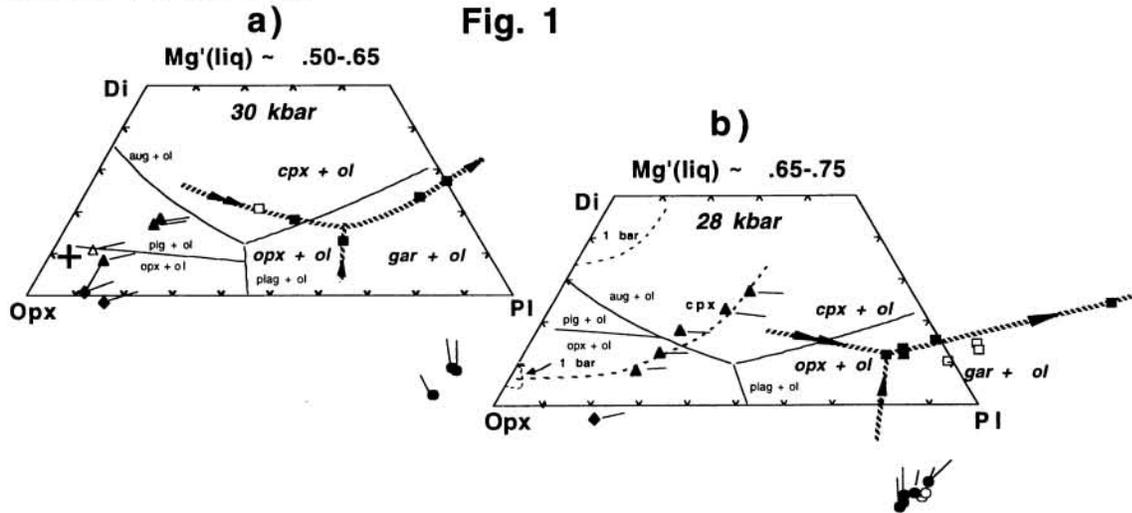


Fig. 2

